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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Serial No.: 10/051,228

Group Art Unit: 1775

Inventors: Thomas A. Taylor et al.

Filed: January 22, 2002

Title: MULTILAYER THERMAL
BARRIER COATING

Examiner: Jennifer McNeil

ARGUMENT

Certificate of Transmission

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Sir:

This is in response to the Office Action mailed September 22, 2004.

Reconsideration of this application is respectfully requested in view of the comments that follow. Applicants acknowledge with appreciation the allowability of claims 5, 6, 14 and 15.

Unobviousness of Applicants' claimed invention can best be appreciated by a thorough understanding the problem that faced Applicants and the unexpected solution discovered by Applicants.

The Problem

In a gas turbine engine, there are blades and air (gas) seals in the compressor section of the gas turbine, whose purpose is to increase the pressure and temperature of the air by multiple blade stages and deliver warm-high-pressure air to the combustor. In the combustor section, fuel is injected and the fuel-air mixture burned to produce very hot, even higher pressure gaseous combustion products. The hot-high-pressure combustion products exit the combustor and work to rotate the blades in the turbine section, where the thermal energy is thus converted to mechanical energy.

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In addition to operating a gas turbine engine at high gas temperatures, there are other factors that contribute to engine efficiency. One of these is the amount of air in the compressor section or combustion gas in the turbine section that flows over the tips of the blades or vanes rather than flowing over the blade airfoil surfaces. Minimizing this amount increases the turbine efficiency. This is accomplished by placing radially adjacent to the tips of the rotating blades, but slightly spaced away from the tips, an outer gas seal ring or segments of a ring. These rings or segments are stationary and are set to have as small a gap between the surface of the gas seal and the rotating blade tips as possible. The smaller the gap, the less leakage of the high-pressure gas from one turbine or compressor stage to the next. A similar situation exists between rotating knife edges and inner gas seals on stationary vanes.

The gap between the gas seal surface and the blade tips (or the knife edges) needs to be minimized to prevent gas pressure leakage between the stages. If the gap is set too close, then it is possible that the blade tips may rub the gas seal surface. This may occur due to increased blade length due to thermal expansion or to centrifugal forces resulting from the high rotation speed. If the gap is set too loose, such that a tip rub would never occur, engine efficiency is sacrificed. In the case of a rub, either the blade tip or the gas seal surface or both will experience wear. Wear results in the loss of material from the blade or air seal. Material loss primarily from the blade tip has the effect of permanently increasing the gap. Wear loss mainly from the gas seal is more desirable. Gas seals are designed slightly wider than the blade width so that a wear track in the air seal is a groove as wide as the blade tip chord, but with some material at the leading and trailing edges of the air seal not rubbed. This groove provides a labyrinth-like flow path for the high pressure gas that does not result in as much gas pressure drop as would occur if the same amount of wear were all on the blade tip. So it is preferred that the wear be primarily into gas seal segment surfaces and minimized on blade tips.

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It is possible to force the majority of wear to the gas seal segment by coating it with an abradable coating, and coating the blade tip with a wear-resistant coating, or even an abrasive tip coating. It is advantageous, particularly in the turbine section where it may even be necessary, for the abradable to also be a thermal barrier coating to protect the metallic seal substrate. This increases the efficiency of the engine by either allowing higher gas operating temperatures or by reducing the amount of bypass cooling air necessary to keep the seal segments within their allowable operating temperature range.

Many attributes may have to be met simultaneously by a coating on a seal segment or ring including, as noted above, that it may have to be both abradable and a thermal barrier. The abradability of a material is a function of a number of factors including the material's mechanical strength, density, friability, temperature of operation, nature of interacting at its rub surface, etc. Laboratory scale rub tests have been developed to help guide the choice of material for its abradability. The results of all testing to date have shown that the amount and distribution of wear depend not only on the material providing the abradable gas seal, but also on the material on the rubbing tip.

The effective thickness of most thermal barriers is limited because their thermal shock resistance decreases as their thickness increases. Yet, thicker ceramic coatings are desired for gas seals to meet increasing thermal insulation requirements, allow for greater incursion of the blade tips or other wear and to have enough material initially present to allow the gas seal ring to be case-ground to a final dimension. The latter is particularly important when the gas seal ring is ground to a diameter, the origin of which is offset from the mechanical center of the ring.

The cited reference, Taylor et al. (U.S. Pat. No. 5,073,433), discloses a relatively dense ceramic thermal spray coating, generally using yttria-stabilized zirconia. The microstructure of this coating, utilizes vertical crack segmentation to enhance thermal shock and thermal fatigue resistance. Furthermore, this coating has

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little long-range internal stress and by itself can be coated to very high thickness and still be resistant to thermal shock. The major impediment to utilizing this coating as a gas seal is its high density and, hence, its limited abradability.

The Solution

Applicants have discovered coatings that are excellent thermal barriers, excellent abradables, or both. In addition, Applicants have discovered coatings that facilitate depositing much thicker thermal barrier coatings than previously was possible; and these thicker coatings retain excellent thermal shock and thermal fatigue resistance not possible with conventional thermal barrier coatings. The coatings comprise multiple layers of ceramic materials with different microstructures that provide the coating system with much greater thermal shock resistance. The ceramic materials used by Applicants are usually oxides, most often based on zirconia, and are thus capable of operation at high temperatures, such as those obtained in the high temperature turbine section of gas turbine engines. The coating systems may also find utility in the compressor section of gas turbine engines and in other applications.

Low density oxide coatings, particularly low density zirconia coatings, are good thermal barriers and may have good abradability, but even with a metallic bondcoat they usually do not have adequate thermal shock and thermal fatigue resistance, if they are more than about 20 mils (0.5 mm) thick. Thicker coatings are required for many applications, for example in gas turbine engines to provide adequate thermal protection and to provide adequate thickness to allow for initial grinding to design tolerances and to allow for incursion of the blade tips and other wear. This is particularly true for coatings used as abradable thermal barriers on seals in gas turbine engines. Advantageously, Applicants have discovered a coating system that has an outer layer of low density oxide, particularly low density zirconia, that is a good abradable thermal barrier and that may be substantially thicker than 20 mils (0.5 mm) and still have adequate thermal shock and thermal fatigue resistance. This is especially surprising since Applicants' inner ceramic layer has a plurality of

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macrocracks distributed throughout, wherein the macrocracks comprise vertical segmentation macrocracks that extend at least one half the thickness of the inner ceramic layer and there are from about 7.5 to 75 vertical macrocracks per linear centimeter of coating width. With such coatings, one would expect spallation and vertical crack propagation and separation under thermal shock and fatigue conditions.

Applicants have found that coatings with multiple layers, wherein an inner layer between the substrate or bondcoat and the low density oxide outer layer has a unique macrocracked microstructure, can be produced with an unusually thick low density top or outer layer coating and still retain adequate thermal shock and thermal fatigue resistance. This is most unexpected, since it would normally be thought that cracks would lead to spallation of the top layers of a coating under conditions of thermal shock or thermal fatigue such as those experienced in gas turbine engines. In such coatings with multiple layers, Applicants have surprisingly found no spalling, no vertical crack propagation, and no vertical crack separation under severe thermal shock testing. See, for example, Example 2 in Applicants' specification.

It has been found that at least one of the macrocracked microstructures of the multilayer coating can be advantageously deposited in a thick layer that retains high thermal shock and thermal fatigue resistance. If the inner layer is composed of two or more sublayers of differently macrocracked microstructures, then the coating may have even greater thermal shock and thermal fatigue resistance. For example, the inner layer may include a first cracked layer and a second cracked layer. Additional inner ceramic layers of varied macrocrack orientations and densities can provide incremental increases to the multilayer coating's life. For example, alternating between inner ceramic layers containing only vertical macrocracks and layers containing both vertical and horizontal macrocracks may further increase the multilayer coating's life.

The Examiner is directed to the limitations included in Applicants' claims that set forth the discoveries made by Applicants. Applicants point out that the

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instant claims relate to multilayer ceramic coating for providing thermal barrier protection to a gas turbine outer air seal that opposes a blade tip or knife edge, said multilayer ceramic coating comprising an inner ceramic layer coating the gas turbine outer air seal, the inner ceramic layer having a plurality of macrocracks distributed throughout the inner ceramic layer, wherein the macrocracks comprise vertical segmentation macrocracks that extend at least one half the thickness of the inner ceramic layer and there are from about 7.5 to 75 vertical macrocracks per linear centimeter of coating width, and an outer ceramic abradable layer coating the inner ceramic layer, the outer ceramic abradable layer being substantially free of vertical macrocracks, and wherein said multilayer ceramic coating has a high speed tip-to-seal wear ratio of 0.1 or less, a thickness of at least about 0.2 mm, and cyclic thermal shock resistance up to a temperature of at least about 2500°F.

Applicants further point out that the instant claims relate to gas turbine outer air seal having a multilayer ceramic coating for providing thermal barrier protection to at least a portion of the gas turbine outer air seal, the multilayer ceramic coating comprising an inner ceramic layer coating the gas turbine outer air seal, the inner ceramic layer having a plurality of cracks distributed throughout the inner ceramic layer, wherein the cracks comprise vertical segmentation macrocracks that extend at least one half the thickness of the inner ceramic layer and there are from about 7.5 to 75 vertical macrocracks per linear centimeter of coating width, and an outer ceramic abradable layer coating the inner ceramic layer, the outer ceramic abradable layer being substantially free of vertical macrocracks, and wherein said gas turbine outer air seal opposes a blade tip or knife edge and said multilayer ceramic coating has a high speed tip-to-seal wear ratio of 0.1 or less, a thickness of at least about 0.2 mm, and cyclic thermal shock resistance up to a temperature of at least about 2500°F.

The Rejections

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The rejection of claims 1, 3, 4, 9-13, 17-25, 27-30, 32-35, 37 and 38 under 35 U.S.C. 103(a) as being unpatentable over Taylor et al. (US 5,073,433) in view of Graham et al. (US 6,432,487) is respectfully traversed.

The rejection of claims 1, 3, 4, 9-13, 17-25, 27-30, 32-35, 37 and 38 under 35 U.S.C. 103(a) as being unpatentable over Taylor et al. (US 5,073,433) in view of Good et al. (US 6,358,002) is respectfully traversed.

The rejection of claim 26 under 35 U.S.C. 103(a) as being unpatentable over Taylor et al. (US 5,073,433) and Good et al. (US 6,358,002) and further in view of Gupta et al. (US 5,403,669) is respectfully traversed.

The Arguments for Unobviousness

The primary reference, Taylor et al. discloses a thermal barrier coating comprising zirconia partially stabilized by yttria and having a substantial homogeneous dispersion of vertical macrocracks throughout the coating to improve its thermal fatigue resistance. As noted by the Examiner in the Office Action, Taylor et al. does not disclose "an additional coating thereon that does not include macrocracks". Nowhere does Taylor et al. disclose or suggest a multilayer ceramic, thermal barrier and abradable coating for a gas turbine outer air seal that opposes a blade tip or knife edge, the coating comprising an inner ceramic layer having specifically defined vertical macrocracks distributed throughout and an outer ceramic abradable layer substantially free of vertical macrocracks and having a high speed tip-to-seal wear ratio of 0.1 or less, and the coating having a thickness of at least about 0.2 mm and cyclic thermal shock resistance up to a temperature of at least about 2500°F, as claimed by Applicants.

The secondary reference, Graham et al., adds nothing to make up for the deficiencies of Taylor et al. as a primary reference. Graham et al. discloses a process for applying a vertically cracked ceramic thermal barrier coating to a machine component by applying a plurality of layers of the ceramic thermal barrier coating on the component utilizing a nozzle at a first distance from the

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component, applying an additional sacrificial outer layer of the ceramic thermal barrier coating of the same chemical composition as the plurality of layers on the component with the nozzle at a second distance from the component, and removing at least some of the outer layers to achieve desired thickness and surface roughness specifications.

Graham et al. discloses only vertically cracked ceramic thermal barrier coatings in general and is silent with respect to an outer layer that does not include vertical cracks and has a high speed tip-to-seal wear ratio of 0.1 or less. Further, in contrast to Applicants' claimed invention, Graham et al. is also silent with respect to ceramic thermal barrier coatings having a thickness of at least about 0.2 mm, the coatings having cyclic thermal shock resistance up to a temperature of at least about 2500°F, and the length and frequency (i.e., number of vertical cracks per linear centimeter of the coating) of the vertical cracks included in the ceramic thermal barrier coatings. While Graham et al. discloses a thin outer layer for finishability to some smoothness by blending with diamond impregnated disks, Applicants' claimed invention provides multilayer ceramic coatings capable of high speed tip rub abradability, i.e., a high speed tip-to-seal wear ratio of 0.1 or less. Nowhere does Graham et al. disclose or suggest a multilayer ceramic, thermal barrier and abradable coating for a gas turbine outer air seal that opposes a blade tip or knife edge, the coating comprising an inner ceramic layer having specifically defined vertical macrocracks distributed throughout, wherein the cracks comprise vertical segmentation macrocracks that extend at least one half the thickness of the inner ceramic layer and there are from about 7.5 to 75 vertical macrocracks per linear centimeter of coating width, and an outer ceramic abradable layer substantially free of vertical macrocracks and having a high speed tip-to-seal wear ratio of 0.1 or less, and the coating having a thickness of at least about 0.2 mm and cyclic thermal shock resistance up to a temperature of at least about 2500°F, as claimed by Applicants.

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The secondary reference, Good et al., adds nothing to make up for the deficiencies of Taylor et al. as a primary reference. Good et al. discloses a gas turbine engine air seal coated with an alumina base layer, over which is applied a relatively dense and erosion resistant ceramic layer. The seal also includes a porous abradable ceramic layer applied over a portion of the erosion resistant ceramic layer. Microcracks can form in and extend generally through the dense ceramic layer. Good et al. does not disclose or suggest vertical segmentation macrocracks that extend at least one half the thickness of the inner ceramic layer and there are from about 7.5 to 75 vertical macrocracks per linear centimeter of coating width as required by Applicants' claimed invention. Nowhere does Good et al. disclose or suggest a multilayer ceramic, thermal barrier and abradable coating for a gas turbine outer air seal that opposes a blade tip or knife edge, the coating comprising an inner ceramic layer having specifically defined vertical macrocracks distributed throughout, wherein the cracks comprise vertical segmentation macrocracks that extend at least one half the thickness of the inner ceramic layer and there are from about 7.5 to 75 vertical macrocracks per linear centimeter of coating width, and an outer ceramic abradable layer substantially free of vertical macrocracks and having a high speed tip-to-seal wear ratio of 0.1 or less, and the coating having a thickness of at least about 0.2 mm and cyclic thermal shock resistance up to a temperature of at least about 2500°F, as claimed by Applicants.

The secondary reference, Gupta et al., adds nothing to make up for the deficiencies of Taylor et al. as a primary reference. Gupta et al. discloses thermal barrier coatings applied to metal substrates for high temperature exposure protection and in which a bond coating is disposed between the substrate and thermal barrier coating. The bond coating is applied with an outer portion of a surface roughness in the range of about 200-600 microinches Roughness Average (Ra), and the diffusion of Al into such portion is stated to substantially retain such

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surface roughness as an anchor for a subsequently applied thermal barrier coating. Nowhere does Gupta et al. disclose or suggest a multilayer ceramic, thermal barrier and abradable coating for a gas turbine outer air seal that opposes a blade tip or knife edge, the coating comprising an inner ceramic layer having specifically defined vertical macrocracks distributed throughout, wherein the cracks comprise vertical segmentation macrocracks that extend at least one half the thickness of the inner ceramic layer and there are from about 7.5 to 75 vertical macrocracks per linear centimeter of coating width, and an outer ceramic abradable layer substantially free of vertical macrocracks and having a high speed tip-to-seal wear ratio of 0.1 or less, and the coating having a thickness of at least about 0.2 mm and cyclic thermal shock resistance up to a temperature of at least about 2500°F, as claimed by Applicants.

Applicants submit that alleged obviousness of the instantly claimed invention must be predicated on something more than it would have been obvious to try adding an outer ceramic abradable layer substantially free of vertical macrocracks and having a high speed tip-to-seal wear ratio of 0.1 or less (in contrast to the sacrificial outer layer of Graham et al.), to a single layer thermal barrier coating having vertical macrocracks that extend at least one half the thickness of the inner ceramic layer and there are from about 7.5 to 75 vertical macrocracks per linear centimeter of coating width, to arrive at Applicants' claimed multilayer ceramic coatings for a gas turbine outer air seal that opposes a blade tip or knife edge or the possibility that such a particularly defined multilayer ceramic coating would have been considered in the future, having been neglected in the past. See Ex parte Argabright et al. 161 USPQ 703. It is submitted that "obvious to try" is not a valid test of patentability, and patentability determinations based on that as a test are contrary to statute. See In re Mercier 515 F2d 1161, 185 USPQ 774; In re Antonie 559 F2d 618, 195 USPQ 6; In re

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Goodwin et al. 576 F2d 375, 198 USPQ 1; and In re Tomlinson et al. 363 F2d 928, 150 USPQ 623.

Clearly, it is only by hindsight that the Examiner could impute to the single layer, vertically cracked, thermal barrier coatings of Taylor et al. (e.g., a single layer thermal barrier coating having vertical macrocracks that extend at least one half the thickness of the inner ceramic layer and there are from about 7.5 to 75 vertical macrocracks per linear centimeter of coating width) an outer ceramic abradable layer substantially free of vertical macrocracks and having a high speed tip-to-seal wear ratio of 0.1 or less (in contrast to the sacrificial outer layer of Graham et al.) to arrive at the instantly claimed multilayer ceramic coatings for a gas turbine outer air seal that opposes a blade tip or knife edge, and such hindsight obviousness after the invention has been made is not the proper test. See In re Carroll 601 F2d 1184, 202 USPQ 571.

In view of the above arguments, the rejections are deemed improper and should be withdrawn.

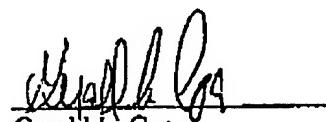
It is respectfully submitted that the rejections of record are improper and that the application is in condition for allowance. Accordingly, reconsideration and allowance of all claims are courteously solicited.

A response to the Office Action mailed September 22, 2004 was due December 22, 2004. Accordingly, submitted herewith is a petition for an extension of time for three (3) months. Please charge fees/surcharge which may

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be required by this paper, or credit any overpayment, to Deposit Account No. 16-
2440.

Respectfully submitted,



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